

A NEW METHOD FOR THE SIMULTANEOUS DETERMINATION OF PYRITE CONTENT AND PROXIMATE ANALYSIS IN COAL

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ABSTRACT

The development of a new simultaneous method for the determination of pyrite content and proximate analysis in coal is presented. It combines thermogravimetry and thermomagnetometry and utilizes inert, oxidizing and reducing gases. Results by the new technique are compared to the ASTM method, with the proximate analysis being obtained on a Fisher coal analyzer and pyrite content reported by the Coal Research Section of the Pennsylvania State University. Comparison of the thermomagnetogravimetry technique (TMG) with the ASTM method indicates good agreement and comparable accuracy.

These studies show that TMG for proximate analysis and pyrite contents in coal is a viable, accurate alternative to the present, more cumbersome ASTM methods. The principle advantages of thermomagnetogravimetric technique are: (1) ease of determination of both proximate analysis and pyrite, which permits the use of unskilled technicians; (2) widespread availability of the apparatus; (3) cost effectiveness due to use of unskilled operators; (4) automation, presently available for proximate analysis on some commercial instruments and is easily accomplished for pyrite analysis, as well; (5) possible advantage over the pyrite analysis by the ASTM method in two situations: first, when pyrite is totally surrounded by acid-insoluble organic material, and second, where significant amounts of pyrite have weathered to FeSO_4 ; and (6) a permanent record of the continuous measurements is made, in contrast to the ASTM method which records only initial and final conditions.

INTRODUCTION

The American Society for Testing Materials (ASTM) has established procedures for the determination of proximate analysis of coal [1]. These have been used for some time and a great deal of empirical data based on them has been collected. However, the ASTM-recommended procedures for proximate analysis are tedious and time-consuming, and require considerable skill on the part of the operator.

Sulfur in coal has received much attention because of its environmental impact. It is desirable to know the pyrite content in addition to the total sulfur. As with proximate analysis, the ASTM procedure for pyrite analysis is cumbersome, and measures iron, not sulfur [2]. Alternatives to the ASTM

test for pyrite have been proposed, using combined X-ray fluorescence and diffraction [3], Mössbauer spectroscopy [4] and γ -ray absorption [5]. However, X-ray diffraction is rather inaccurate, Mössbauer spectroscopy is even harder to quantitate, and the γ -ray technique requires elaborate irradiation and counting facilities.

During the past several years, thermogravimetry (TG) has been proposed independently by several groups as a preferred technique for proximate analysis of coal. Fyans [6] first used TG for proximate analysis; however, this was published in a Perkin-Elmer applications reprint which was overlooked by some workers. Elder [7] used similar instrumentation to analyze coals. TG was independently proposed [8–10] for proximate analysis and Ottaway [11] and Earnest and Fyans [12] also contributed further measurements. All of these works showed excellent agreement with ASTM measurements, even though different conditions were used by the various researchers using TG.

Hyman and Rowe [8] proposed combined thermogravimetry–thermomagnetometry (TMG) as an alternative to the ASTM method for measuring the pyrite content in addition to proximate analysis. TMG equates the amount of pyrite present with the amount of easily oxidizable and reducible iron compounds present.

The purpose of this work is to further test the Hyman–Rowe [8] method and to present results for the combined proximate analysis and pyrite content of coal.

EXPERIMENTAL

The thermomagnetic balance used in this work was a Cahn RG-2000 equipped with a 4600 Oe permanent magnet with pole faces shaped for Faraday analysis. The system has been described elsewhere [8].

A coal sample was placed in a quartz or platinum crucible, suspended from the balance in a furnace, and analyzed as shown schematically in Fig. 1. The figure shows a thermogram indicating the gas flow through the furnace. After sample insertion, the system was closed to the atmosphere and the initial weight, W_i , of the sample recorded (region A in Fig. 1). It was then flushed with dry nitrogen for at least 10 min at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ to purge the system of oxygen. The magnetic field was applied to the sample to check for possible initial magnetism, indicative of Fe_2O_3 , then removed. Normally, W_{im} is virtually identical with W_i (Fig. 1).

Proximate analysis

The furnace was then turned on and the temperature was raised with a heating rate of about $35^\circ\text{C min}^{-1}$ to 105°C and held there to drive off the

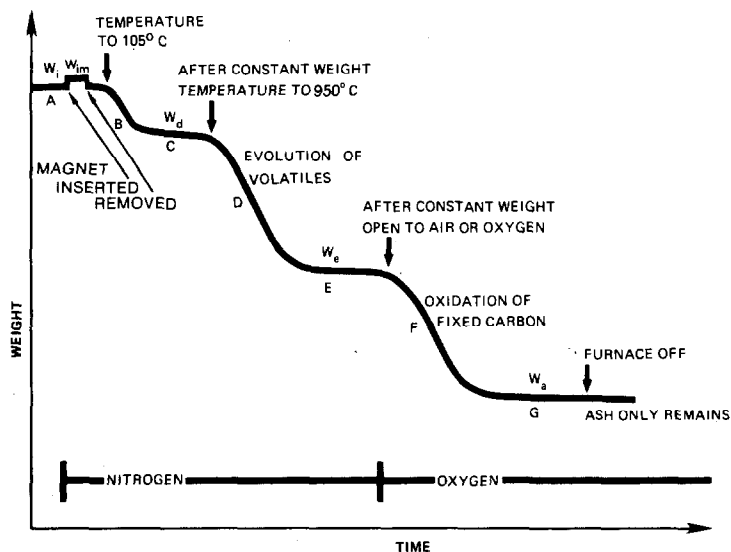


Fig. 1. Schematic diagram illustrating the procedure for determining proximate analysis of coal or lignite by thermogravimetry.

moisture, resulting in weight loss (region B, Fig. 1). After 8–10 min at 105°C , the weight became constant and was recorded as the dry weight (W_d , region C). The temperature was then raised at about $100^{\circ}\text{C min}^{-1}$ to 750°C and held for 7 min. Although the furnace used was limited to an upper limit of 750°C and sometimes temperatures even lower than 750°C were used with reasonable results, it is recommended that the temperature used in the ASTM method for proximate analysis be used for the corresponding step in the TG procedure. Thus, 950°C is recommended for the removal of volatiles and $700\text{--}750^{\circ}\text{C}$ for the determination of fixed carbon. Elder [7] and Ottaway [11] used 900 and 900°C , respectively, for these two temperatures and Earnest and Fyans [12] used 950 and 950°C , respectively. All these researchers obtained good agreement with known values. After 7 min, the weight, W_e , was virtually constant and was used to calculate the % volatile matter (point E). The loss in weight in moving through region D corresponded to the loss of the volatile matter. At E, air was allowed to flow through the system at a rate of $50\text{ cm}^3\text{ min}^{-1}$, which oxidized the remaining organic matter, causing the weight loss observed in region F. The weight loss represents the fixed carbon of the sample. When only ash remained, the weight again became constant (W_a , region G) and the furnace was turned off. After cooling to $\leq 150^{\circ}\text{C}$, hydrogen was allowed to flow through the system at a rate of $50\text{ cm}^3\text{ min}^{-1}$ to prepare for the pyrite analysis.

Pyrite analysis

After 10 min H_2 flow, the sample was analyzed for pyrite as illustrated schematically in Fig. 2, which is a continuation of the thermogram shown in Fig. 1. The magnet was again placed so that it acted on the sample, which resulted in an apparent weight increase (region H) due to the saturation magnetization of Fe_2O_3 ($0.1-0.5 \text{ emu g}^{-1}$), the oxidation product of pyrite. The temperature was raised to 400°C at a rate of $\sim 100^\circ\text{C min}^{-1}$ with the hydrogen flowing, which caused the reduction of Fe_2O_3 to metallic iron. This yielded a large apparent weight increase (region I) since the saturation magnetization of Fe ($218 \text{ emu}^{-1} \text{ g}$) is much larger than that of Fe_2O_3 . When the reduction was complete, as indicated by the apparent weight once again becomes constant (region J), the furnace was turned off. Upon cooling, the saturation magnetization increased (region K), until the sample approached room temperature, where the apparent weight, W_{fm} , became constant (region L). The magnet was removed and the weight of the residue, W_f , was recorded (region M).

Data reduction

Proximate analysis data were calculated from the information in Fig. 1 in the usual way.

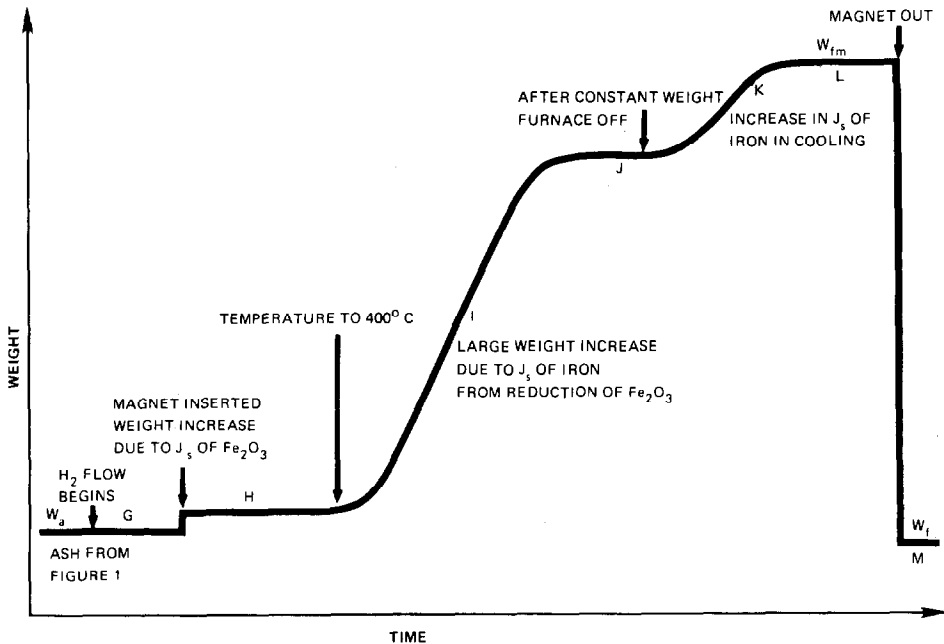


Fig. 2. Schematic diagram illustrating the procedure for analyzing the pyrite content of coal or lignite by thermomagneto-gravimetric analysis (TMG).

The pyrite content was calculated from

$$\% \text{ pyrite} = \frac{(W_{fm} - W_f)}{J_0(\text{Fe})} \times \frac{FW(\text{FeS}_2)}{AW(\text{Fe})} \times \frac{100\%}{W_d} = 0.985 \frac{(W_{fm} - W_f)}{W_d} \quad (1)$$

where W_{fm} = apparent weight of the reduced ash in the magnetic field, W_f = weight of the reduced ash, $FW(\text{FeS}_2)$ = formula weight of FeS_2 , $AW(\text{Fe})$ = atomic weight of iron, $J_0(\text{Fe})$ = saturation magnetization of Fe, and W_d = dry weight of the sample. If the sample was measurably magnetic at the beginning of the analysis, i.e., $W_{im} > W_i$ in Fig. 1, then it was concluded that hematite, Fe_2O_3 , was present initially. Unless accounted for, this could cause an error in the pyrite determination. Since the pyrite was oxidized to Fe_2O_3 during the proximate analysis, the apparent weight of the ash in the magnetic field, W_{am} (i.e., apparent weight at H in Fig. 2), represents Fe_2O_3 from pyrite plus any initial Fe_2O_3 . The fraction P of Fe due to the pyrite could then be calculated from:

$$P = (W_{am} - W_{im}) / W_{am} \quad (2)$$

Multiplying this fraction by W_{fm} in eqn. (1) would correct for iron initially present as Fe_2O_3 .

Sample description

The coal samples used in this work, and their description, were provided by C. Philip Dolsen of the Coal Research Section of the Pennsylvania State University and are shown in Table 1. The samples were received in physical forms varying from coarse powders to chunks ~ 1 mm in diameter. All samples were ground in a tungsten carbide shatter box to allow passage through a 120-mesh screen. No more than 2 min grinding was necessary to ensure that the bulk of the sample would pass through the 120-mesh screen. Material that did not pass through the 120-mesh screen was ground and sieved again until all material had passed through. The sample was then remixed by placing it in a round-bottom flask and putting it on a wrist-action shaker for 2 h.

RESULTS

The 30 coal samples studied here were analyzed in quintuplicate by thermomagnetogravimetry (TMG) and in duplicate for the proximate analysis on a Fisher (model 490) coal analyzer (FCA) over a short time period, i.e., within a week or two. This allowed direct comparison of the TMG results with the accepted ASTM-modified method of the FCA [13]. In addition, quintuplicate pyrite analyses via TMG were determined to be compared with results supplied by the Pennsylvania State University Coal

TABLE 1

Brief description of coal and lignite samples received from the Coal Research Laboratory of the Pennsylvania State University

Sample	Apparent rank	Sample type	Seam name	Sample location
PSOC241	subB	Channel whole seam	Monarch	Sheridan Co., WY
PSOC260	mvB	Channel whole seam	Middle Kittanning	Clearfield Co., PA
PSOC284	hvAb	Channel whole seam	Lower Dekoren	Williamson Co., IL
PSOC286	hvBb	Channel whole seam	Tebo	Henry Co., MO
PSOC319	lvB	Channel whole seam	Upper Kittanning	Somerset Co., PA
PSOC347	hvAb	Channel subsection	Lower Kittanning	Clarion Co., PA
PSOC350	hvAb	Channel subsection	Lower Clarion	Clarion Co., PA
PSOC425	subC	Channel whole seam	Unnamed	Freestone Co., TX
PSOC459	hvBb	Channel subsection	Lower Sunnyside	Emery Co., UT
PSOC535	subA	Channel subsection	Dietz	Big Horn Co., MT
PSOC540	hvCb	Channel subsection	Wadge	Routt Co., CO
PSOC593	hvCb	Channel lithotype bright coal	Illinois No. 5	Fulton Co., IL
PSOC595	hvCb	Channel whole seam	Indiana No. 7	Warrick Co., IN
PSOC625	ligA	Channel lithotype	Darco	Harrison Co., TX
PSOC633	lvB	Channel whole seam	No. 1 Seam	Lycoming Co., PA
PSOC636	subC	Channel whole seam	Wildcat	Milam Co., TX
PSOC639	subC	Channel lithotype	Wildcat	Milam Co., TX
PSOC650	lvB	Channel whole seam	Paris	Logan Co., AR
PSOC707	hvC	Channel subsection	Pittsburg	Braxton Co., WV
PSOC715	hvAb	Channel whole seam	Redstone	Lewis Co., WV
PSOC726	hvAb	Channel whole seam	Sewell "B"	Randolf Co., WV
PSOC752	hvAb	Channel subsection	Ohio No. 6	Tuscarawas Co., OH
PSOC762	hvAb	Channel subsection	Ohio No. 5	Coshocton Co., OH
PSOC764	hvAb	Channel subsection	Ohio No. 6	Tuscarawas Co., OH
PSOC828	hvCb	Channel whole seam	Brazil Block	Parke Co., IN
PSOC837	subC	Channel whole seam	Pust	Richland Co., MT
PSOC872	an	Run of mine	Buck Mountain	Luzerne Co., PA
PSOC1036	ligA	Channel whole seam	Unnamed	Panola Co., TX
PSOC1185	hbB	Channel whole seam	Illinois No. 5	Perry Co., IL

TABLE 2

Proximate analysis: as received results

Sample PSOC No.	% Moisture		% Volatile matter		% Ash		% Fixed carbon		% Pyrite	
	FCA*	TMG**	FCA	TMG	FCA	TMG	FCA	TMG	PSU	TMG
241	13.2	14.1±0.9	42.7	39.0±0.5	6.7	6.5±0.2	50.6	54.4±0.3	0.86	0.81±0.01
260	1.1	1.1±0.1	24.0	23.8±0.3	9.6	8.9±0.2	66.4	66.3±0.6	4.96	5.50±0.09
284	4.7	5.3±0.3	37.4	37.4±0.5	20.1	20.2±0.5	42.5	42.5±0.4	7.56	7.47±0.13
286	6.5	7.2±0.5	34.5	33.5±0.4	27.4	25.9±0.7	38.7	40.3±0.9	7.97	6.30±0.13
319	2.8	2.6±0.2	19.4	19.4±0.3	17.7	17.0±0.5	63.0	63.5±0.7	10.98	10.51±0.14
347	2.0	2.5±0.2	39.2	39.5±0.5	7.7	8.9±0.2	53.2	51.6±0.4	4.86	2.31±0.10
350	2.3	2.4±0.2	38.5	38.2±0.5	11.0	12.3±0.3	50.5	49.6±0.3	6.60	6.70±0.22
425	20.7	21.1±1.4	47.4	46.5±0.6	10.2	10.2±0.3	42.4	42.8±0.2	0.49	0.12±0.01
459	5.0	4.4±0.3	38.7	38.4±0.5	9.2	10.1±0.3	52.0	51.5±0.4	0.36	0.77±0.02
535	16.2	16.6±0.9	42.7	41.2±0.6	7.2	7.3±0.2	50.1	51.3±0.7	0.71	1.06±0.03
540	8.3	8.7±0.5	38.4	38.4±0.5	11.9	12.1±0.3	49.7	49.5±0.4	1.44	1.45±0.03
593	7.5	6.8±0.4	37.2	36.0±0.5	9.2	8.6±0.2	53.7	55.6±0.8	2.75	2.48±0.15
595	8.3	8.4±0.5	36.9	37.1±0.5	14.9	15.2±0.4	48.1	47.7±0.7	8.21	7.93±0.04
625	10.5	12.1±1.8	43.4	43.6±0.6	17.7	16.6±0.4	38.9	39.2±0.8	0.95	1.00±0.05
633	1.8	1.7±0.1	19.0	19.6±0.3	11.5	12.1±0.3	69.6	70.0±0.4	3.29	3.95±0.06
636	16.0	16.4±0.9	48.1	47.8±0.6	15.9	16.8±0.5	36.0	35.5±0.3	1.63	1.75±0.04
639	11.8	12.0±0.8	50.4	49.8±0.7	23.8	23.7±0.6	25.8	26.4±0.3	1.80	1.41±0.10
650	1.9	2.0±0.1	18.6	19.6±0.3	20.2	19.1±0.5	61.2	61.6±0.3	1.63	1.74±0.04
707	2.5	2.8±0.2	37.8	37.7±0.5	5.7	5.9±0.2	56.5	56.4±0.5	2.75	3.00±0.14
715	3.5	3.7±0.2	39.1	39.4±0.5	6.9	7.2±0.2	53.8	53.4±0.3	2.34	2.56±0.10
725	1.3	1.6±0.1	29.1	28.2±0.4	7.6	8.7±0.2	63.3	63.2±0.9	2.88	3.02±0.16
726	1.3	1.1±0.1	31.2	30.4±0.5	4.5	4.2±0.1	64.3	65.4±0.5	0.71	0.17±0.01
752	4.2	4.7±0.3	41.3	41.8±0.4	8.6	9.1±0.2	50.3	49.1±0.5	0.84	1.12±0.06
762	4.9	4.9±0.3	38.3	38.3±0.4	12.9	10.2±0.3	50.3	51.5±0.6	8.87	9.59±0.13
764	4.7	4.7±0.3	49.6	47.2±0.4	6.7	6.6±0.2	50.7	50.7±0.7	2.45	2.48±0.09
828	9.6	9.8±0.6	40.4	40.7±0.5	6.5	6.8±0.2	53.2	52.5±0.5	1.05	1.47±0.02
837	29.5	29.1±1.8	42.5	43.4±0.3	12.6	13.0±0.3	44.9	43.9±0.4	0.32	0.89±0.02
872	5.5	5.3±0.3	2.3 ^a	1.7±0.4 ^a	4.4	5.0±0.2	92.0	93.3±0.6	0.02	0.34±0.01
1036	27.5	28.3±0.8	45.8	44.9±0.7	11.6	11.7±0.3	42.9	43.4±0.5	0.21	0.32±0.01
1185	6.9	6.8±0.3	36.1	35.1±0.3	11.7	9.8±0.2	55.0	57.1±0.6	3.63	3.76±0.4

^a Because of expanded scale for % volatile matter, PSOC-872 values were not plotted in Fig. 3.

Research Laboratory. The averages of these measurements are given in Table 2.

Moisture

Comparison of the moisture analyses by TMG with the Fisher coal analyzer is shown in Table 2. Agreement is satisfactory. Our TMG results

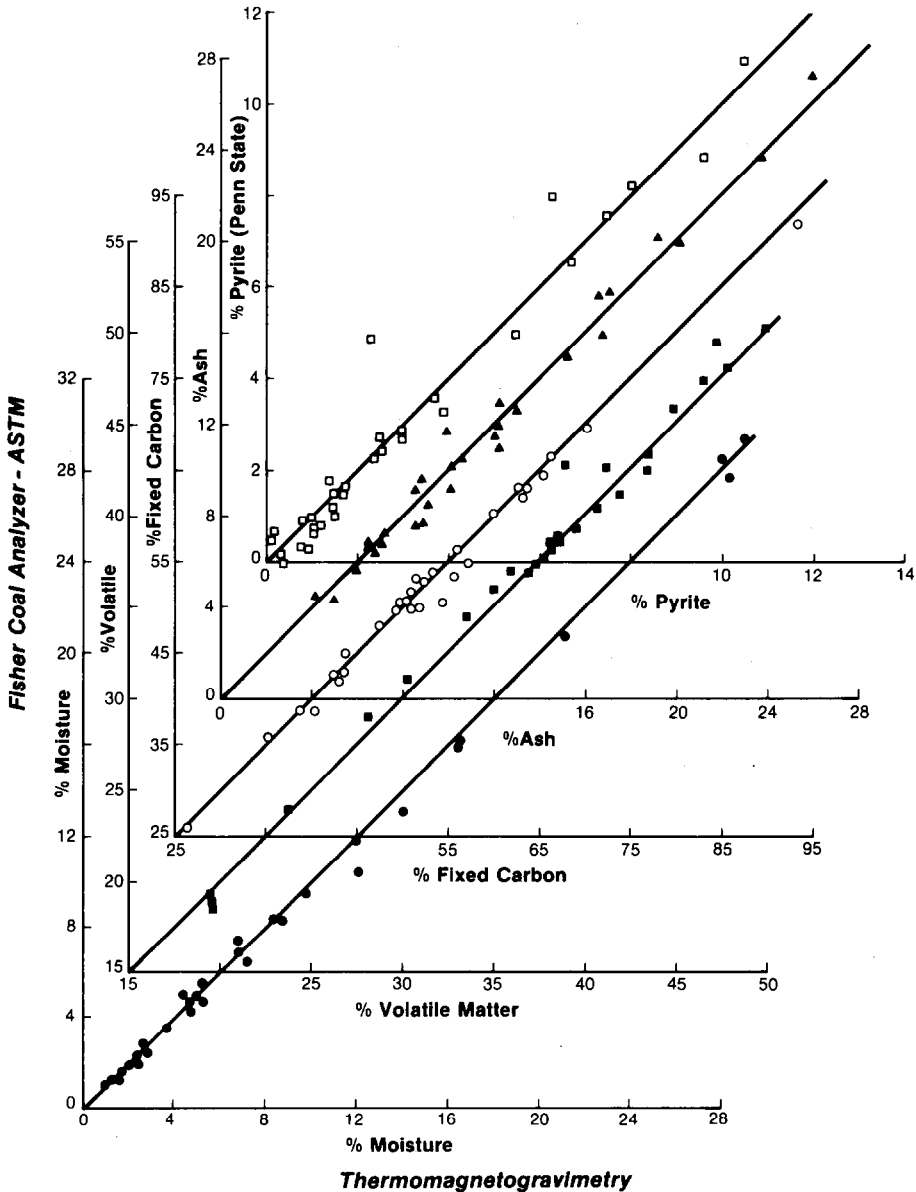


Fig. 3. Plot of the results by thermogravimetric analysis compared to those obtained using the Fisher coal analyzer.

appear to be systematically higher by about 3% relative to those of the FCA. The TMG average of five measurements of each sample, along with the standard error of the mean, σ/\sqrt{N} , is shown in Table 2. Figure 3 includes a graph of the TMG values vs. the FCA results of moisture in the 30 coal samples. It can be seen from the lower plot in Fig. 3 that a 45° line is obtained with relatively little scatter about the line.

Volatile matter determination

Table 2 also includes a comparison of the volatile matter from the TMG and FCA techniques. Agreement between the two is good, generally agreeing within the estimated precision (see Table 2). There are no systematic errors greater than perhaps 1% in the TMG compared to the ASTM analysis of volatile matter, even at the greatly reduced temperature. Volatile matter determinations using the ASTM procedure are rigidly specified as to heating rate and temperature, as are the other parameters of the proximate analysis. The temperature used here (only 750°C and sometimes less) is much lower than in the FCA (950°C) and the heating rate much more rapid; from 105 to 750°C in ~6 min, a rate of ~100°C min⁻¹ compared to a 35°C min⁻¹ heating rate with the FCA. However, disparity in temperature and heating rate did not produce any substantial difference in the volatile matter determinations of the two techniques. Figure 3 also includes a graph of the TMG data on volatile matter compared to the FCA values. The points define a line with a slope of 1.01, confirming general agreement within about ±1%.

Fixed carbon determination

In TMG, the fixed carbon is determined directly by the observation of weight loss going from the volatile-free weight to ash weight. In the ASTM procedure it is calculated by difference. In both cases, proximate analysis must total 100%. Thus, in the ASTM method, all factors that cause errors in moisture, volatile matter, and ash determinations will contribute as added error in the fixed carbon measurement. Nonetheless, as seen in Table 2, agreement between the two methods is quite good and the results are compared graphically in Fig. 3. Here, the average precision (one standard deviation) for the two methods, TMG and FCA, were calculated to be virtually identical, about ±0.6–0.7%.

Ash determination

Again, as illustrated in Table 2, TMG results compare fairly well with the FCA values. The average ratio of TMG/FCA results differ by less than 1% so that, here, too, there is no significant systematic error observed. Figure 3 includes a graphical display of the comparison.

An occasional problem occurred with the Fisher coal analyzer, i.e., the incomplete oxidation of some samples in spite of the higher temperatures used. Sometimes, when the ash was removed from the FCA sample crucible, black carbonaceous material was found under the lighter colored ash. Since the sample obviously had not completely oxidized, results from those determinations were discarded and the samples were reanalyzed. Incomplete oxidation was not observed with TG.

Pyrite content determination

As mentioned earlier, pyrite determination by TMG adds only 45 min or less to the time required for the proximate analysis and follows it naturally. The ASTM analysis, which requires that the sample be digested, filtered, treated with several reagents, and then titrated, takes much longer [2]. It also demands a skilled technician, whereas TMG needs a relatively unskilled person. For instance, six graduate students in the chemistry department with no previous experience with thermal analysis were given 10 min instruction and requested to conduct duplicate analyses of proximate analysis and pyrite analysis in a coal. Their results agreed in every case within the estimated uncertainty with the results we obtained by TG and with the FCA.

The inorganic sulfur in coal occurs predominantly as iron sulfides, primarily FeS_2 , marcasite or pyrite, which differ only in structure, occasionally as pyrrhotite, and as FeSO_4 which is the product of air oxidation of FeS_2 and occurs when coal or lignite are exposed to weathering.

Care must be taken in the ASTM method for pyrite analysis to ensure that pyrite grains surrounded by organic matter are totally extracted because the HNO_3 may not easily penetrate the organic layer to dissolve the pyrite. However, Suhr and Given [14] show that with careful application of the ASTM procedure, no major errors were encountered. Also, in the ASTM method, pyrite which has weathered to FeSO_4 is not analyzed since the FeSO_4 is removed by washing with HCl , a procedure intended to remove non-pyritic iron.

Table 2 compares the results of the pyrite determinations of 25 coal samples analyzed in this work by TMG and five conducted earlier by Hyman and Rowe [8] to the present results from the Coal Research Laboratory of the Pennsylvania State University. TMG pyrite results on only six of the samples, PSOC numbers 350, 540, 625, 752, 828 and 1185, needed to be corrected for the presence of initial Fe_2O_3 according to eqn. (2).

As can be seen from an examination of Table 2 and visually exhibited in Fig. 3, there is general agreement between the pyrite results taken by our new TMG technique and those by the ASTM method. The agreement is not as close as was observed for proximate analysis. However, it should be noted that our proximate analysis values determined by the TMG method agreed better with the data from the Fisher coal analyzer than with those reported

from the Pennsylvania State University Coal Research Section, both of which used ASTM accepted methods. Thus, it is not clear whether the lack of agreement which is observed in the pyrite values between our laboratory and those from the Pennsylvania State University is due to an increase in the uncertainty in our values or theirs. At any rate, the agreement is rather more encouraging than not and further work will be necessary to elucidate the causes of the few large discrepancies which are seen.

CONCLUSIONS

The results presented here show that thermomagnetogravimetry (TMG) is an advantageous alternative to the currently used ASTM standard methods for the proximate analysis and the pyrite content determination of coal. The use of TMG for the proximate analysis yields results which are directly comparable to those obtained using the ASTM procedures, in a fraction of the time (45 min or less vs. 5 h). The repeatability of the TMG method compares reasonably well with the ASTM tests, and could potentially be improved through precise microprocessor control of the temperature and heating rate. Microcomputer controls could also be used to automate the process. The fact that in TMG analyses both pristine pyrite and that which has been oxidized to FeSO_4 may be taken as an advantage or a disadvantage, depending upon the information desired. Our method yields the total pyrite content prior to oxidation. However, distinguishing between these two forms of iron is an indication of how oxidized a coal has become. Our method also records pyrite which may not be leached from the sample by nitric acid and would, hence, go unobserved in the ASTM determination. Furthermore, TMG determination of pyrite is simpler than the ASTM method and requires very little sample preparation. TMG can be performed using commonly available instrumentation, and ease of the analysis allows for the use of unskilled operators.

The disadvantage of using TMG for coal analysis, as performed here, is the small size of the sample that can be analyzed. With powdering and sieving to 120-mesh, this does not constitute a real disadvantage for proximate analysis. The size of the crucible used here was limited by the necessity of constructing the sample heater tube with a diameter that would fit between the poles of the magnet, about 20 cm. The crucible had to be small enough to hang inside the tube without touching the walls of the tube. Employing a larger magnet, i.e., an electromagnet, could allow the use of a larger sample, which would possibly reduce the standard deviation of the technique. In particular, sampling error may explain the larger spread in the pyritic comparison.

To summarize, the utilization of TMG for proximate analysis and pyrite content determination has a number of advantages over the methods cur-

rently recommended by the ASTM: (1) the simplicity and speed of the analysis; (2) the widespread availability of the apparatus; (3) low cost; (4) potential for automating the process; (5) this method may be superior for the analysis of pyrite in coal samples in which a substantial portion of the pyrite is encased in organic matter or clayey minerals; and (6) a permanent, continuous record is retained unlike the ASTM method which records only initial and final values.

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